Pathways to the Oxidation of Copper

Scientific Achievement

X-ray scattering studies at the Advanced Photon Source (APS) have demonstrated the importance of investigating oxygen-induced surface structures in-situ, under equilibrium conditions of temperature and oxygen partial pressure (pO_2). We have determined the equilibrium pO_2-T phase diagram for the Cu (001) surface for the first time and are making significant progress towards understanding the effects of surface structure on the subsequent nucleation behavior of oxide islands of interest, for example, as heterogeneous catalysts. We observe two oxygen-ordered structures, with a $\left(2\sqrt{2}\times\sqrt{2}\right)R45°$ missing-row reconstruction stable below approximately 100°C and a c(2x2) structure stable at higher temperatures. A two-phase region separates these phase fields on the equilibrium surface phase diagram. Transitions between these phases are fully reversible, demonstrating that these are stable rather than metastable structures. Furthermore, based both on diffraction peak intensity measurements and observations of crystal truncation rod (CTR) intensity under variable pO_2, we find that oxygen surface coverage is also reversible, meaning that an oxygen-free metal surface is recovered when temperature is increased sufficiently and/or pO_2 is reduced below an equilibrium phase boundary. We also find that, as pO_2 is increased to the point at which Cu_2O islands nucleate, these oxide islands co-exist and interact with the c(2x2)-structured surface regions. For example, Cu_2O islands will temporarily stabilize the c(2x2) structure even under reducing conditions; the c(2x2) structure disappears only after complete reduction of the oxide islands.

Significance

Since Cu_2O islands nucleate on the reconstructed surface, the insights provided by these observations are critical to understanding Cu oxidation behavior. This knowledge in turn, is impacting our understanding of the effects of temperature and pO_2 on the reactivity of Cu surfaces for applications such as catalysis (*e.g.*, oxidation of CO or reforming of hydrocarbons to produce hydrogen). The thermodynamics of the oxygen-reconstructed Cu (001) surface have attracted much scientific interest, but previous results have often reached conflicting conclusions, with some studies claiming a $\left(2\sqrt{2}\times\sqrt{2}\right)R45°$ structure is stable and others reporting instead that a c(2x2) structure is "the" stable surface phase. A common feature of past studies is that samples were dosed with oxygen at elevated temperatures, but then were cooled to room temperature for observation under UHV conditions. The present study is the first time that the Cu (001) surface structure has been characterized under non-vacuum conditions and thus is the first to recognize that these two structures are stable under different conditions of temperature and pO_2.

Performers

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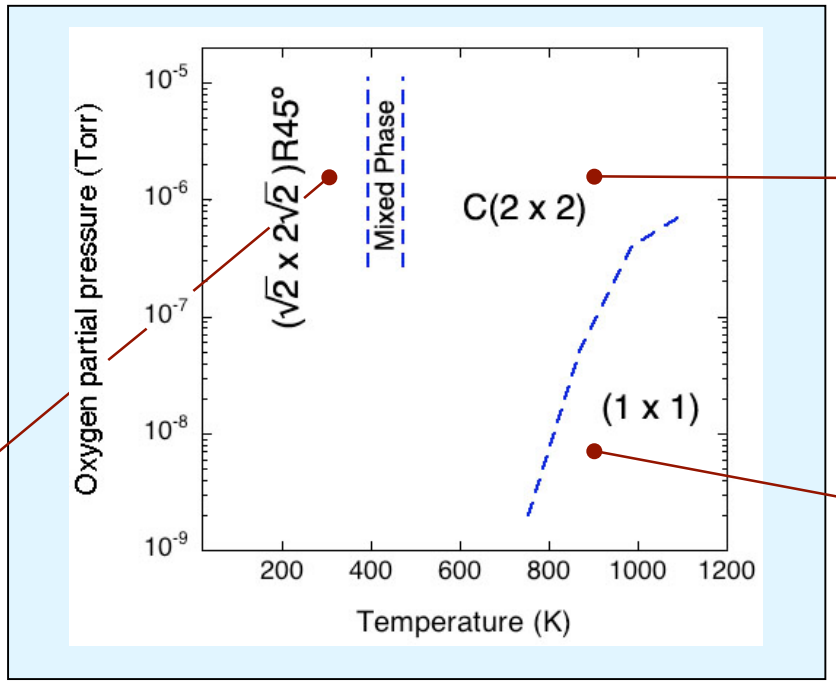
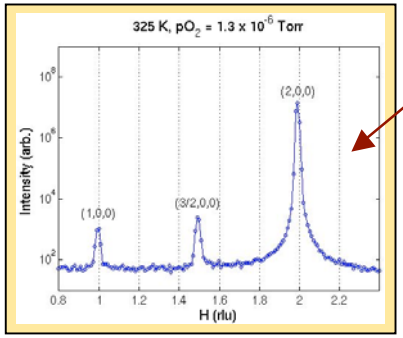
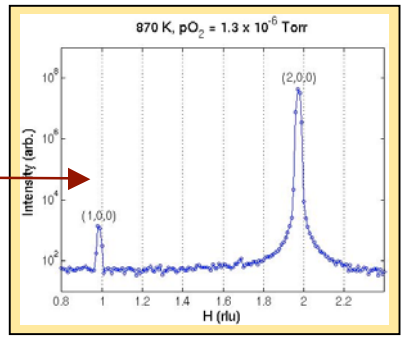
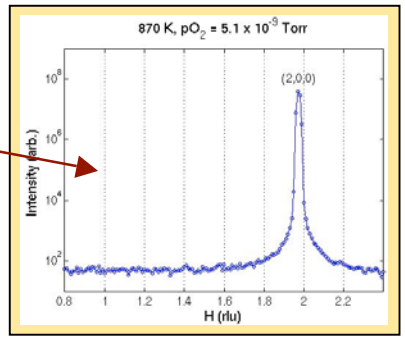
Determination of T- and pO_2- dependent structure provides insight into important surface properties

In-situ x-ray studies have resolved a controversy on the first step of Cu (001) oxidation: two surface phases are stable at different T and pO_2









Our observations were made in-situ, under equilibrium conditions of temperature and oxygen partial pressure. Previous studies reached conflicting conclusions regarding surface phase stability because samples were dosed with oxygen at high T, but then were observed far from equilibrium at low T under UHV conditions.

- Initial surface structure impacts subsequent nucleation and growth of oxide islands; knowledge from in-situ studies is critical to gaining a predictive understanding of oxidation processes.
- These results also provide insight into the effects of T and pO_2 on reactivity of Cu surfaces for applications such as catalysis.

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